ALUMINA COMPOSITES WITH SOLID LUBRICANT PARTICIPATIONS,
SINTERED BY SPS-METHOD

The paper presents the sintering results of Al$_2$O$_3$-Ti(C,N) ceramics with the additions of solid lubricant materials. Al$_2$O$_3$-Ti(C,N) based ceramics with solid lubricating substances were sintered by the SPS-method. In the phase known as lubricants, the following materials were used: MoS$_2$, WS$_2$, CaSO$_4$, SrSO$_4$ and MoO$_2$ and CaO. The Al$_2$O$_3$-Ti(C,N) ceramics were also prepared with the addition of TiB$_2$. The SPS-sintered materials were characterized by values of relative density from 93 to 99%. In the case of the addition of 10 and 30% TiB$_2$, the relative density, Young’s modulus and hardness HV1 were close or equal to the values of the base material. For other additions, the Young’s modulus ranged from 74 to 83% and hardness from 62 to 76% of the Young’s modulus and hardness value for the base material. Regardless of the additive or its volume, the fraction of the friction coefficient was 49 to 86% of the friction coefficient value for the base material. Taking into account the value of the friction coefficient and the physical and mechanical properties, the most promising material is a ceramic with the addition of TiB$_2$ or MoO$_2$ with CaO.

Keywords: alumina, SPS sintering, hardness, density, Young Modulus, friction coefficient

CERAMIKA Al$_2$O$_3$-Ti(C,N) Z DODATKAMI STAŁYCH SUBSTANCJI SMARUJĄCYCH,
SPIEKANA METODĄ SPS

Prezentowano wyniki badań dotyczących spiekania ceramiki o osnowie Al$_2$O$_3$-Ti(C,N) z dodatkami faz pośredzkowych. Scharakteryzowano właściwości mechaniczne i tribologiczne wytworzonych materiałów. Spośród faz określanych jako pośredzowe do badań wykorzystano następujące materiały: MoS$_2$, WS$_2$, CaSO$_4$, SrSO$_4$ oraz MoO$_2$ i CaO. Biorąc pod uwagę niski współczynnik tarcia ceramiki o osnowie TiB$_2$, wytworzono również ceramikę Al$_2$O$_3$-Ti(C,N) z dodatkiem wysokotlenowej fazy TiB$_2$. Materiały spiekane metodą SPS odznaczały się wartością gęstości względnej od 93 do 99%. W przypadku materiałów z dodatkiem 10 i 30% TiB$_2$ wartości gęstości względnej, modułu Younga oraz twardości HV1 były zbliżone bądź równe wartościom materiału bazowego. Dla pozostałych dodatków moduł Younga wynosił od 74 do 83%, a twardość od 62 do 76% wartości modułu i twardości materiału Al$_2$O$_3$-Ti(C,N). Niezależnie od rodzaju dodatku i jego udziału objętościowego obniżono współczynnik tarcia od 49 do 86% wartości współczynnika tarcia materiału bazowego. Najniższą wartość współczynnika tarcia zmierzono dla materiału po spiekaniu SPS z dodatkiem WS$_2$. Materiał ten jednak odznaczał się względnie niskim modułem Younga oraz twardością. Biorąc pod uwagę wartość współczynnika tarcia oraz właściwości fizyczne i mechaniczne, najbardziej obiecującym materiałem jest ceramika z dodatkiem TiB$_2$ oraz MoO$_2$ i CaO.

Słowa kluczowe: ceramika Al$_2$O$_3$, spienie SPS, twardość, gęstość, moduł Younga, współczynnik tarcia

INTRODUCTION

Carrying out the machining process without the use of liquid cooling lubricants results in a reduction in investment and production costs. A reduction in friction and the elimination of fluids from the production process can be achieved by coating the tool surface or by adding lubricating substances resistant to the action of high temperatures, to the structure of the tool solid. In the case of sliding materials, it is not sufficient that the material have a layered crystal structure. The prerequisite is the existence in such a structure of weak bonds between the layers [1, 2].

Another well-known and commonly used lubricating agent is molybdenum disulphide, which, like graphite, has a layered structure and is characterised by a low coefficient of friction. The low coefficient of friction of MoS$_2$ is maintained up to 200°C [3]. In the case of a WS$_2$ based sliding phase, decomposition occurs at a little higher a temperature (approx. 450°C), whilst complete oxidation does not occur even when the temperature is raised to 600°C. The MoS$_2$ lubricant layers can also be produced with the use of chemical or mechanical methods as described in papers [4, 5].

In the case of high-speed machining, solid sliding agents should be characterised by a low friction coefficient and resistance to oxidation at temperatures exceeding 800°C. In such a case, the layers are composed of high- and low-temperature phases, which, as a result of the reaction to temperature and friction, become
more temperature stable phases. In accordance with this mechanism, phases can be formed which are characterised by good tribological properties at high temperatures, for example: PbMoO$_4$ and ZnWO$_4$ (MoS$_2$ + PbO→PbMoO$_4$; WS$_2$+ZnO→ZnWO$_4$) [6]. On the basis of the mechanical and tribological studies results presented in [7], it may be stated that the content of sliding agents in tool ceramics should not exceed 10%.

Among those materials characterised by a higher temperature resistance than graphite or MoS$_2$, worthy of mention are: CaSO$_4$, BaSO$_4$ and SrSO$_4$. As stated in other works [7, 8], sulphate-based sliding phases are characterised by a lower friction coefficient, even at temperatures of around 600°C. The high temperature resistance and good tribological properties of SrSO$_4$ layers are confirmed by the results presented in paper [9]. PbMoO$_4$, ZnMoO$_4$ and ZnWO$_4$ layers have similar properties (friction coefficient, wear resistance, high-temperature wear resistance). At low temperatures, sulphate-based sliding layers and those containing MoO$_4^{2-}$ or WO$_4^{2-}$ ions are characterised by a higher friction coefficient and are rapidly damaged. This is confirmed by the results of the tribological studies presented in paper [7]. A promising material for use in tool ceramics as a solid lubricating agent is BaCrO$_4$. This phase is characterised by a low and constant friction coefficient over a wide temperature range, up to approximately 800°C. ZrO$_2$(Y$_2$O$_3$)-BaCrO$_4$ ceramics produced by SPS (Spark Plasma sintering) are characterised by a higher resistance to abrasive wear, in comparison to ZrO$_2$(Y$_2$O$_3$)-base ceramics [10].

**EXPERIMENTAL**

Materials and procedure

The Al$_2$O$_3$-Ti(C,N) ceramics with the addition of various lubricating substances were subjected to investigation. The base material was composed of the following powders: Al$_2$O$_3$ (A16SG, ALCOA) with the addition of ZrO$_2$ (FLUKA) and with the addition of 25 vol.% Ti(C,N) (H.C. STARCK). The average sizes of the Al$_2$O$_3$; ZrO$_2$ and Ti(C,N) particles were smaller than 1 μm.

Al$_2$O$_3$-Ti(C,N) base ceramics with the addition of solid lubricating substances were sintered by the SPS method.

To the base material were added:
1. 10 vol.% CaSO$_4$ (POCH)
2. 10 vol.% SrSO$_4$ (POCH)
3. 10 vol.% WS$_2$ (WP-801, AEE, 1–5 μm)
4. 10 vol.% MoS$_2$ (Mo-801, AEE, 1–5 μm)
5. 10 vol.% TiB$_2$ (HC STARCK, 2.5–3.5 μm)
6. 30 vol.% TiB$_2$ (HC STARCK, 2.5–3.5 μm)
7. 10 vol.% MoO$_3$ (POCH) + CaO (POCH)

The materials for SPS sintering were pressed in a graphite die with a pressure of 35 MPa and in vacuum conditions. The maximum pressure was obtained after 10 minutes. Vacuum and pressure time (10 minutes) are needed to vent the mixture in the graphite die. The sintering process was operated in a nitrogen atmosphere.

The sintering parameters for Al$_2$O$_3$-Ti(C,N) base ceramics with additives were determined with respect to the melting point of the solid lubricant materials. The sintering parameters are presented in Table 1. The shrinkage of those materials during the sintering process is shown as graphs in Figures 1-3.

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**Fig. 1.** Shrinkage of materials sintered by SPS-method: 1 - Al$_2$O$_3$-Ti(C,N); 2 - Al$_2$O$_3$-Ti(C,N)+10%TiB$_2$; 3 - Al$_2$O$_3$-Ti(C,N)+30%TiB$_2$

Rys. 1. Zmiana objętości materiałów w trakcie procesu spekania: 1 - Al$_2$O$_3$-Ti(C,N); 2 - Al$_2$O$_3$-Ti(C,N)+10%TiB$_2$; 3 - Al$_2$O$_3$-Ti(C,N)+30%TiB$_2$

**Fig. 2.** Shrinkage of materials sintered by SPS-method: 1 - Al$_2$O$_3$-Ti(C,N); 2 - Al$_2$O$_3$-Ti(C,N)+MoS$_2$; 3 - Al$_2$O$_3$-Ti(C,N)+WS$_2$; 4 - Al$_2$O$_3$-Ti(C,N)+MoO$_3$+CaO

Rys. 2. Zmiana objętości materiałów w trakcie procesu spekania: 1 - Al$_2$O$_3$-Ti(C,N); 2 - Al$_2$O$_3$-Ti(C,N)+MoS$_2$; 3 - Al$_2$O$_3$-Ti(C,N)+WS$_2$; 4 - Al$_2$O$_3$-Ti(C,N)+MoO$_3$+CaO

**Fig. 3.** Shrinkage of materials sintered by SPS-method: 1 - Al$_2$O$_3$-Ti(C,N); 2 - Al$_2$O$_3$-Ti(C,N)+CaSO$_4$; 3 - Al$_2$O$_3$-Ti(C,N)+SrSO$_4$

Rys. 3. Zmiana objętości materiałów w trakcie procesu spekania: 1 - Al$_2$O$_3$-Ti(C,N); 2 - Al$_2$O$_3$-Ti(C,N)+CaSO$_4$; 3 - Al$_2$O$_3$-Ti(C,N)+SrSO$_4$
TABLE 1. Sintering parameters of Al₂O₃-Ti(C,N) base ceramic with additives ($T_s$ - melting point; $P_{max}$ - max. pressure; $T_{\text{max}}$ - temperature at max. pressure; $T_s$ - sintering temperature; $t_s$ - sintering time; $P_n$ - pressure at sintering temperature)

<table>
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<th>Additives</th>
<th>$T_s$ °C</th>
<th>$P_{max}$ MPa</th>
<th>$T_{\text{max}}$ °C</th>
<th>$T_s$ °C/°s</th>
<th>$P_n$ MPa</th>
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<td>35</td>
<td>1100</td>
<td>1500/60</td>
<td>10</td>
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<tr>
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<td>1500</td>
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<td>35</td>
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<tr>
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<td>1000</td>
<td>1500/60</td>
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<td>10</td>
</tr>
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</table>

Methodology

After sintering, the materials were subjected to a study of their physical and mechanical properties. The apparent density $\rho_a$ was measured using the hydrostatic method. Young's modulus measurements of the sintered samples were also taken, using the ultrasonic method of measuring the transition speed of transverse and longitudinal waves, using a Panametrics Epoch III flaw detector. The hardness was determined by the Vickers method at a load of 9807 mN using a digital hardness tester (Future Tech. Corp. FM-7) The tribological studies were performed using a UMT-T2 universal testing machine. Analysis of the tribological properties of the individual materials was performed at a temperature of 22°C and the friction radius was in the range of 3 to 5 mm. The force of the counter-sample on the tested material was 10 N, the speed of the sample was 0.100 m/s and the friction road was 100 m. The physical, mechanical and tribological investigations were performed on the samples with a ground and polished surface.

Results of investigations

The results of the measurements of density, Young’s modulus and Vickers hardness are contained in Table 2. The results of the measurements of the friction coefficient for Al₂O₃-Ti(C,N) base ceramics with solid lubricant participation are contained in Table 3.

The SPS sintered materials were characterized by the values of relative density from 93 to 99%. In the case of the TiB₂ addition, the relative density, Young’s modulus and hardness HV1 were close or equal to the values of the base material. For the other additives, the Young modulus ranged from 74 to 83% and hardness from 62 to 76% of the value for the base material, Al₂O₃-Ti(C,N).

Table 2 presents the measurement results of relative density, the Young modulus and hardness which were recorded for the base material Al₂O₃-Ti(C,N) after sintering by the SPS-method with parameters similar for materials with solid lubricant additives. The base material sintered at reduced parameters was marked by the lowest relative density, Young's Modulus and hardness.

The materials with low melting phases exhibited better sinterability than the base material, by increasing the presence of diffusion in the liquid phase, as evidenced by the curves shown in Figures 2 and 3.

Application of the SPS method made it possible to lower the temperature of sintering of the base ceramics Al₂O₃-Ti(C,N) and significantly shorten the time of this process. The materials after sintering by SPS had a modified surface layer with a high content of graphite, which must be removed by grinding.

Based on the results of the tribological investigations, it was found that the additives induce a lower friction coefficient. The values of this coefficient for materials with solid lubricant additives after SPS sintering ranged from 49 to 86% of the coefficient for the base materials. The lowest value of the friction coeffi-
cient (0.25) was measured for the material with the WS$_2$ phase. A low friction coefficient was also observed for the materials with 10% TiB$_2$ and 30% TiB$_2$, and with the addition of MoO$_3$ and CaO, which were characterized by the best mechanical properties.

Taking into account the value of the friction coefficient and the physical and mechanical properties, the most promising material is a ceramic with the addition of TiB$_2$ or MoO$_3$ with CaO.

### CONCLUSIONS

Presented in this study are the results of the mechanical and tribological studies of Al$_2$O$_3$-Ti(C,N) base ceramics with additives to reduce friction resistance. Irrespective of the type of additive, it was possible to reduce the friction coefficient to between 49 and 86% of the base material coefficient.

The lowest friction coefficient was measured for the material after SPS sintering with WS$_2$; but this material was characterized by a relatively low Young's Modulus and hardness.

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### REFERENCES


